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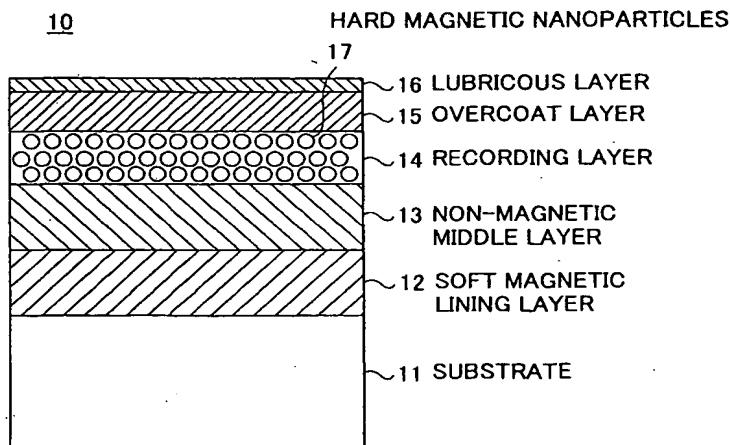
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### (54) A perpendicular magnetic memory medium, a manufacturing method thereof, and a magnetic memory storage

(57) A perpendicular magnetic memory medium capable of high-density recording and reproducing consists of a soft magnetic lining layer (12), a non-magnetic middle layer (13), a recording layer (14) that is formed by arranging hard magnetic nanoparticles (17), an overcoat layer (15), and a lubricous layer (16), all of which are arranged on a substrate (11) in this sequence, wherein an average diameter of the nanoparticles rang-

es between 2nm and 10nm, a standard deviation of diameters of the nanoparticles is 10% or less of the average diameter of the nanoparticles, and an average interval of the nanoparticles is between 0.2 nm and 5 nm, and an magnetic easy axis of the recording layer 14 is perpendicular to a face of the substrate (11), such that high-density recording and reproducing is realized by the perpendicular magnetic medium.

FIG.1



**Description****BACKGROUND OF THE INVENTION****1. Field of the Invention**

**[0001]** The present invention generally relates to a perpendicular magnetic memory medium, a manufacturing method thereof, and a magnetic memory storage that contains the perpendicular magnetic memory medium, and especially relates to a perpendicular magnetic memory medium that is suitable for high-density recording and reproducing, a manufacturing method thereof, and a magnetic memory storage that contains the perpendicular magnetic memory medium.

**2. Description of the Related Art**

**[0002]** In recent years, the memory capacity of a magnetic memory storage has greatly expanded, the physical dimensions thereof are remarkably becoming small, and the recording density of, e.g., a magnetic disk drive of an in-plane magnetic memory is growing at an annual rate of 100%.

**[0003]** Since it is envisaged that a perpendicular magnetic memory provides a recording density that is far higher than the in-plane magnetic memory, because adjacent magnetized regions do not interfere with each other, generating little influence of an anti-magnetic field, the perpendicular magnetic memory is drawing attention again.

**[0004]** In order to enhance the recording density of the perpendicular magnetic memory medium, medium noise of a recording layer has to be reduced, while securing a signal output. To achieve this, the diameter of crystal nanoparticles of a hard magnetic metal thin film used for a recording layer has to be fine and uniform. Conventionally, the thin film of a CoCr system alloy has been used as the recording layer. In order that the diameter of the nanoparticles is made small, elements such as V, Nb, and the like have been added to the CoCr system alloy. However, controlling the distribution of the diameter of the nanoparticles has been a difficult matter, with the diameter becoming smaller and smaller, making it difficult to manufacture a recording layer suitable for further higher-density recording.

**[0005]** As a technique for comparatively easily obtaining hard magnetic nanoparticles of a minute and uniform diameter for a recording layer, a chemical method has been proposed by Sun et al. in Science, 287th volume No.17 (2000) pp.1989, and by JP,2000-54012,A. According to the method, the hard magnetic nanoparticles are compounded chemically, and are autonomously orientated by the intermolecular force, thereby the hard magnetic nanoparticles, which are orderly oriented, are obtained. In the recording layer, wherein the nanoparticles are oriented in this manner, a nanoparticles exchange interaction and a magnetostatic interaction are

reduced, and medium noise is decreased. However, since these interactions are reduced, the thermal stability of the recorded magnetization is deteriorated.

**[0006]** In order to improve the thermal stability, it is considered necessary that a material that has high magnetic anisotropy energy be used. Ordered alloys, such as FePt, CoFe, and FePd, are being studied as the material.

**[0007]** Nanoparticles of such as FePt, if compounded chemically by the above-mentioned technique, have low magnetic anisotropy energy and low coercivity, and the nanoparticles compounded by the above-mentioned technique cannot be used for recording and reproducing. Then, in order to raise the magnetic anisotropy energy, heat treatment is performed at a temperature of about 600 degrees C such that the nanoparticles are made an ordered alloy. The heat treatment is carried out in a vacuous environment from a viewpoint of preventing oxidization of the nanoparticles.

**[0008]** However, even if the heat treatment is simply performed, magnetic orientation of the hard magnetic nanoparticles remains random in three dimensions. Therefore, even if the perpendicular recording method is attempted for high-density recording and reproducing, sufficient reproduction output is not obtained, and the high-density recording and reproducing cannot be performed.

**[0009]** Further, the heat treatment deteriorates performances of a soft magnetic lining layer included in the perpendicular magnetic memory medium that is made of a permalloy of poly crystal such as an amorphous material and microcrystal. More specifically, by the heat treatment in high temperatures; coercivity and a magnetic distortion increase, and high frequency characteristics of the soft magnetism of the soft magnetic lining layer deteriorates, hence high-density recording and reproducing cannot be performed.

**[0010]** Furthermore, in the heat treatment at the high temperatures, a glass substrate and an aluminum substrate of the perpendicular magnetic memory medium are softened, and the flatness of the substrate is deteriorated. A reproducing head has to approach the perpendicular magnetic memory medium as close as dozens of nanometers for reproducing high-density recording and reproducing. Perpendicular magnetic memory medium having a poor flatness can cause problems such as a head crash, and the high-density recording and reproducing cannot be performed.

**50 SUMMARY OF THE INVENTION**

**[0011]** Accordingly, the present invention is made in view of the above-mentioned problems, and the objective of the present invention is to provide a perpendicular magnetic memory medium, a manufacturing method thereof, and a magnetic memory storage that contains the perpendicular magnetic memory medium for high-density recording and reproducing, which substantially

obviate one or more of the problems caused by the limitations and disadvantages of the related art.

[0012] Features and advantages of the present invention will be set forth in the description that follows, and in part will become apparent from the description and the accompanying drawings, or may be learned by practice of the invention according to the teachings provided in the description. Objects as well as other features and advantages of the present invention will be realized and attained by the perpendicular magnetic memory medium, the manufacturing method thereof, and the magnetic memory storage that contains the perpendicular magnetic memory medium for high-density recording and reproducing, which are particularly pointed out in the specification in such full, clear, concise, and exact terms as to enable a person having ordinary skill in the art to practice the invention.

[0013] To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described herein, the invention provides the perpendicular magnetic memory medium, the manufacturing method thereof, and the magnetic memory storage that contains the perpendicular magnetic memory medium for high-density recording and reproducing as follows.

[0014] The present invention provides the perpendicular magnetic memory medium that includes a recording layer made of hard magnetic nanoparticles arranged on a substrate, wherein the average of the diameters of the hard magnetic nanoparticles ranges between 2nm and 10nm the standard deviation thereof is less than 10% of the average of the diameter of the nanoparticles, the average interval between the hard magnetic nanoparticles ranges between 0.2nm and 5nm, and the magnetic easy axis of the recording layer is perpendicular to the face of the substrate.

[0015] In the present invention, the diameter of the hard magnetic nanoparticles is made minute, the distribution of diameter of the nanoparticles is controlled, and the average interval between the hard magnetic nanoparticles is controlled to a fixed range. Therefore, the exchange interaction between the hard magnetic nanoparticles and the magnetostatic interaction are suppressed, and the medium noise is reduced. Further, the magnetic easy axis of the recording layer is set perpendicular to the substrate face, i.e., the recording layer has perpendicular magnetic anisotropy, such that sufficient reproduction output is obtained by the perpendicular magnetic memory. High-density recording and reproducing are attained in this manner.

[0016] Here, "the magnetic easy axis of the recording layer is perpendicular to the face of the substrate" means that the magnetic easy axis of each hard magnetic nanoparticle is aligned approximately perpendicular, subject to angle distribution. The angle distribution is expressed by a ratio  $H_{c2}/H_{c1}$ , where  $H_{c1}$  represents perpendicular coercivity that is the coercivity in the perpendicular direction to the substrate face, i.e., the face

of a film of the recording layer, and  $H_{c2}$  represents in-plane coercivity that is the coercivity in the parallel direction to the substrate face. The ratio  $H_{c2}/H_{c1}$  is preferred to be 30% or less, and more preferably, to be 10% or less. Where the ratio is sufficiently small, the width of the magnetization transition region of the remnant magnetism after recording becomes narrow, and the perpendicular magnetic memory medium suitable for high-density recording and reproducing is obtained.

[0017] The hard magnetic nanoparticles of the present invention contain at least two or more elements selected from the group consisting of Fe, Co, Ni, Pt, and Pd.

[0018] The present invention employs alloys, such as FePt and CoPd, for the hard magnetic nanoparticles that form the recording layer. The alloys show ferromagnetism, high magnetic anisotropy energy, and high perpendicular coercivity since the magnetic easy axis is arranged perpendicularly to the substrate. Accordingly, recording bits having a small magnetization transition region are formed, and sufficient reproduction output can be obtained in the high-density recording and reproducing. Further, the alloys can provide stronger coercivity, for example, by heat treatment in a magnetic field, which regularizes an atomic arrangement, and the magnetic easy axis of the hard magnetic nanoparticles can be aligned perpendicularly to the substrate face. Here, the hard magnetic nanoparticles of only one element of Co, Fe, and Ni shows the ferromagnetism, however, magnetic anisotropy energy is not enough to be suitable for the high-density recording and reproducing.

[0019] The present invention provides a soft magnetic lining layer made of an alloy of at least one of Fe, Co, Ni, Al, Si, Ta, Ti, Zr, Hf, V, Nb, C, and B, thereby the magnetic field of a monopole magnetic head is prevented from spreading in the horizontal (in-plane) direction of the recording layer, such that the magnetic field is perpendicularly applied to the recording layer, and a recording bit with a minute magnetization transition region is formed.

[0020] The present invention also provides a manufacturing method of the perpendicular magnetic memory medium, which includes a process wherein magnetism is perpendicularly applied to the recording layer, while heat treatment in a gas atmosphere is applied to the recording layer. The heat treatment process in the magnetic field makes the magnetic easy axis of the recording layer perpendicular to the substrate face.

[0021] In this manner, atoms of the alloy are regularized (ordered alloy is made), and the magnetic easy axis is made perpendicular to the substrate face, providing increased perpendicular coercivity that is suitable for the high-density recording and reproducing.

[0022] The manufacturing method of the present invention provides the heat treatment in the magnetic field, which uses the principle that the higher the gas atmosphere pressure is, the lower the heat treatment temperature is.

**[0023]** The lower temperature of the heat treatment prevents deterioration of the flatness of the recording layer of the memory medium that has desired perpendicular coercivity, and prevents deterioration of the high frequency characteristics of the soft magnetic lining layer.

**[0024]** The heat treatment of the present invention uses a gas that prevents oxidization of the hard magnetic nanoparticles. In this manner, deterioration of the coercivity by oxidization is prevented. Preferably, N<sub>2</sub> gas is used as the gas for the heat treatment. Desired perpendicular coercivity can be obtained at a lower heat treatment temperature.

**[0025]** The present invention also provides the magnetic memory storage equipped with the perpendicular magnetic memory medium according to the present invention.

**[0026]** In this manner, the magnetic memory storage of the present invention is capable of high-density recording and reproducing.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0027]**

Fig. 1 is a sectional view showing a structure of a perpendicular magnetic memory medium of an embodiment of the present invention;  
 Fig. 2 is a view showing a manufacturing process of the perpendicular magnetic memory medium of the embodiment of the present invention;  
 Fig. 3 is a view showing an outline configuration of a spin coater;  
 Fig. 4 is a view showing an outline configuration of a dip coater;  
 Fig. 5 is a sectional view showing a configuration of a heat treatment in magnetic field equipment using a magnet in the normal condition;  
 Fig. 6 is a sectional view showing a configuration of the heat treatment in the magnetic field equipment using a superconductivity magnet;  
 Fig. 7 is a view showing relations between perpendicular coercivity and heat treatment temperatures;  
 Fig. 8 is a view showing relations between a lattice constant of c axis of FePt that constitute hard magnetic nanoparticles and heat treatment temperatures;  
 Fig. 9 is a view showing relations between perpendicular coercivity of the perpendicular magnetic memory medium and N<sub>2</sub> gas atmosphere pressure in the fifth embodiment of the present invention;  
 Fig. 10 is a view showing an X-ray diffraction pattern of the perpendicular magnetic memory medium of the sixth and the seventh embodiments of the present invention;  
 Fig. 11 is a sectional view showing the principal part of an embodiment of the magnetic memory storage; and

Fig. 12 is a plane view showing the principal part of the embodiment of the magnetic memory storage shown in Fig. 11.

**5** **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**[0028]** In the following, embodiments of the present invention will be described with reference to the accompanying drawings.

**[0029]** Fig. 1 is a sectional view of a perpendicular magnetic memory medium 10 of the embodiment of the present invention. As shown in Fig. 1, the perpendicular magnetic memory medium 10 includes a substrate 11, on which a soft magnetic lining layer 12, a non-magnetic middle layer 13, a recording layer 14 that is made of hard magnetic nanoparticles 17, a overcoat layer 15, and a lubricous layer 16 are layered in this sequence.

**[0030]** The substrate 11 is, for example, a crystallized glass substrate, a tempered glass substrate, an aluminum substrate, Si wafer, a plastic substrate, a PET film, and the like. The crystallized glass substrate, Si wafer, and the like, are preferably used from a heat-resistant viewpoint.

**[0031]** The soft magnetic lining layer 12, is made of a soft magnetic material, having thickness between 100 nm and 2 micrometers, and high saturation flux density B<sub>s</sub>, such as amorphous alloys and alloys of a fine crystal of at least one of Fe, Co, Ni, Al, Si, Ta, Ti, Zr, Hf, V, Nb, C, and B, and a laminating film of the alloys. For example, FeAlSi, FeTaC, NiFeNb (B<sub>s</sub>=0.7T), CoCrNb (B<sub>s</sub>=1.2T), and the like are used. The soft magnetic lining layer 12 is formed by a plating method, a sputtering method, a vacuum evaporation method, CVD method (chemical vapor deposit methods), and the like. The soft magnetic lining layer 12 is for absorbing all the magnetic flux from a monopole magnetic head, when recording by the monopole magnetic head. In order to carry out saturation recording, it is desirable that the product of the saturation flux density B<sub>s</sub> and the film thickness is as great as possible. Further, it is desirable that the high frequency characteristics of the soft magnetism, for example, high frequency magnetic permeability, is as high as possible, such that recording at a high transfer speed is obtained. Here, when a ring type head performs recording, it is not necessary to provide the soft magnetic lining layer 12.

**[0032]** The non-magnetic middle layer is 1 nm to 50 nm thick, and is constituted by a non-magnetic material, such as Ti, C, Pt, TiCr, CoCr, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub>. Further, the non-magnetic middle layer 13 may be a laminating film that contains these materials. The non-magnetic middle layer 13 is formed by the sputtering method, the vacuum evaporation method, the CVD method, and the like. The non-magnetic middle layer 13 is formed for, e.g., intercepting magnetostatic interaction of the soft magnetic lining layer 12 and the recording layer 14.

**[0033]** The recording layer 14 includes the hard mag-

netic nanoparticles 17, each of the nanoparticles being of a globular form and the nanoparticles being aligned, and amorphous carbon fills intervals among the hard magnetic nanoparticles 17. Thickness of the recording layer 14 is set between 3 nm and 50 nm. Here, the recording layer 14 may consist of a single layer or a laminating of layers, layered in the direction of the film thickness, of the hard magnetic nanoparticles 17.

[0034] As for the hard magnetic nanoparticles 17, an alloy of materials, such as FePt, FePd, CoPt, and CoPd, is used. The alloy has high magnetic anisotropy energy, providing high perpendicular coercivity. Here, a composition of an alloy is expressed as  $Fe_{100-x}Pt_x$ ,  $Fe_{100-x}Pd_x$ ,  $Co_{100-x}Pt_x$ , and  $Co_{100-x}Pd_x$ , where the suffix indicates a content percentage. It is desirable that X ranges between 20at% and 60at%, more preferably between 35at% and 55a.t%. By setting the composition in the range, high magnetic anisotropy energy is obtained, and high perpendicular coercivity is obtained.

[0035] Furthermore, N, B, C, or P may be added to these alloys as the third element, such that higher magnetic anisotropy energy and higher perpendicular coercivity are obtained.

[0036] The average diameter of the nanoparticles of the hard magnetic nanoparticles 17 is set between 2 nm and 10 nm. If the average diameter of the nanoparticles exceeds 10 nm, the volume of the intervals among the hard magnetic nanoparticles 17, the interval being non-magnetic, becomes large, and a medium noise increases. If the average diameter of the nanoparticles is set to less than 2nm, the hard magnetic nanoparticles 17 tend to become superparamagnetic in the room temperature, and cannot maintain ferromagnetism.

[0037] Further, the standard deviation of the diameters of the hard magnetic nanoparticles 17 is set at 10% or less of the average diameter of the nanoparticles 17. If the standard deviation exceeds 10% of the average diameter of the nanoparticles 17, the distribution of the magnetostatic interaction of the hard magnetic nanoparticles 17 becomes large, and the medium noise increases.

[0038] Furthermore, the average value of the intervals between the hard magnetic nanoparticles 17, i.e., the average interval between the adjacent hard magnetic nanoparticles 17, is set between 0.2 nm and 5 nm. If the average interval exceeds 5 nm, the volume of the interval portion that is non-magnetic between the hard magnetic nanoparticles 17 becomes large, and the medium noise increases, or a reproduction output declines. If the average interval is less than 0.2 nm, the exchange interaction between the hard magnetic nanoparticles 17 increases and the medium noise increases.

[0039] Generally, the magnetic easy axis of the recording layer 14 is perpendicular to the substrate face. In more detail, the magnetic easy axis of each hard magnetic nanoparticles 17 is approximately perpendicular, having angle distribution. The angle distribution is expressed by a ratio  $H_{c2}/H_{c1}$ , where  $H_{c1}$  represents per-

pendicular coercivity, and  $H_{c2}$  represents in-plane coercivity. The ratio is preferably set less than 30%, more preferably less than 10%. In the range, the width of the magnetization transition region of the remnant magnetism after recording becomes narrow, and the perpendicular magnetic memory medium suitable for high-density recording and reproducing is obtained.

[0040] The overcoat layer 15, which is 0.5 nm to 15 nm thick, is constituted from carbon, carbon hydride, carbon nitride, and the like. The overcoat layer 15 is formed by the sputtering method, the CVD method, and the like.

[0041] The lubricous layer 16, which is 0.5 nm to 5 nm thick, is provided on the overcoat layer 15. The lubricous layer 16 is constituted from a lubricant, for example, that contains perfluoro polyether as the main chain, and the like. The lubricous layer 16 is formed by the dipping method, and the like.

[0042] Hereafter, the manufacturing method of the perpendicular magnetic memory medium 10 of the embodiment is explained with reference to Fig. 2 that shows the manufacturing process of the perpendicular magnetic memory medium 10.

[0043] With reference to Fig. 2, the manufacturing process of the perpendicular magnetic memory medium 10 includes a process that prepares a hexane solution of nanoparticles (Step 101 - Step 103), a process that prepares a substrate 21 from the substrate 11 to which the hexane solution of nanoparticles is to be applied (Step 104, and Step 105), and a process that applies the hexane solution of nanoparticles to the substrate 21 such that the recording layer 14 is formed, and heat treatment in a magnetic field is performed, and so on (Step 106 - Step 109).

[0044] First, in the process (Step 101 - Step 103) that prepares the hexane solution of nanoparticles, formation of metal precursor solution (Step 101), generation of nanoparticles (Step 102), and refining of the nanoparticles (Step 103) are performed in this order.

(Formation of metal precursor solution (Step 101))

[0045] At Step 101, Pt complex, for example, 0.5m mol of acetyl acetonat platinum  $Pt(C_5H_7O_2)_2$ , and a reducing agent, for example, 1.5m mol of 1, 2-hexa decandiol are dissolved in  $20cm^3$  of diethyl ether that serves as a solvent at 100 degrees C in an  $N_2$  atmosphere.

[0046] Then, Fe complex, for example, 1m mol of penta carbonyl iron  $Fe(CO)_5$ , and a stabilizer, for example, 0.5m mol of oleic acid, and 0.5m mol of oleyl amine are added. This produces the metal precursor solution. The solution is heated to 297 degrees C, while refluxing and agitating. The composition of the nanoparticles of FePt to be produced is controllable by the ratio of the quantity of Pt complex and Fe complex.

## (Generation of nanoparticles (Step 102))

[0047] Next, the metal precursor solution is agitated for 30 minutes at 297 degrees C, such that nanoparticles are grown up. Thereby, nanoparticles of Fe<sub>50</sub>Pt<sub>50</sub> of 6nm in diameter and 4nm of an average interval are generated. The nanoparticles are stabilized by the stabilizer that covers the surface of the nanoparticles, and the nanoparticles can be handled in air.

[0048] In addition, the average interval between the nanoparticles is controllable by selecting the stabilizer. For example, if hexane acid and hexylamin are used, the average interval of the nanoparticles can be set to 1 nm. Although the nanoparticles will turn into hard ferromagnetism nanoparticles by heat treatment in a magnetic field, as mentioned later, they do not have ferromagnetism at this stage.

## (Refining of the nanoparticles (Step 103))

[0049] Next, a by-product that is synthesized, and remnant (unreacted) agent attached to the nanoparticles are removed. For this purpose, ethanol is added, the nanoparticles are settled and a centrifuge removes supernatant fluid. Furthermore, the nanoparticles are re-distributed in hexane, and ethanol is added. Then, the nanoparticles are settled, and a centrifuge removes supernatant fluid, such that the refinement is performed again.

[0050] Next, with reference to Fig. 2, in the process of preparing the substrate 21 to which the hexane solution of nanoparticles is to be applied, film formation of the soft magnetic lining layer 12 on the substrate 11 (Step 104), and film formation of the non-magnetic middle layer 13 (Step 105) are performed in this order.

## (Film formation of the soft magnetic lining layer (Step 104))

[0051] On the substrate 11, which is, for example, a 2.5 inch Si substrate having SiO<sub>2</sub> formed on its surface by heat oxidization, a film of the soft magnetic lining layer 12 is formed by the plating method, the sputtering method, the vacuum evaporation method, and the like.

## (The non-magnetic middle layer 13 film formation (Step 105))

[0052] A film of the non-magnetic middle layer 13 is formed on the soft magnetic lining layer 12 by the plating method, the sputtering method, the vacuum evaporation method, the CVD method, and the like.

[0053] Next, with reference to Fig. 2, at the process (Step 106 - Step 109) that carries out the heat treatment in the magnetic field, and so on, the hexane solution of nanoparticles is applied (Step 106) to the substrate 21 that has been processed up to the non-magnetic middle layer 13. Then, the heat treatment in the magnetic field

(Step 107) for regularizing the nanoparticles and producing ferromagnetism and perpendicular magnetic anisotropy is performed. Then, film formation of the overcoat layer 15 on the recording layer 14 (Step 108), and application of the lubricous layer 16 to the overcoat layer 15 (Step 109) are performed in this sequence.

## (Application of hexane solution of nanoparticles (Step 106))

[0054] About 1.3cm<sup>3</sup> of hexane solution having a density of 5 mg/cm<sup>3</sup> in which the nanoparticles are re-distributed is applied to the substrate 21 to which the non-magnetic middle layer 13 has been formed, e.g., by a spin coater 30. Fig. 3 shows an outline configuration of the spin coater 30. With reference to Fig. 3, the spin coater 30 includes a feeder 31 that trickles the hexane solution that contains the nanoparticles, and a spindle 32 that rotates the substrate 21. First, the substrate 21 to which the non-magnetic middle layer 13 has been formed is attached to the spindle 32, and the spindle 32 is rotated in the direction of an arrow shown in Fig. 3 at a low speed. After a predetermined amount of the solution is trickled, the spindle 32 is rotated at a high speed in the direction of the arrow, such that the hexane solution is diffused all over the substrate 21. The number of layers of the nanoparticles is controlled by adjusting the rotation speed of the spindle 32, and the density of the hexane solution.

[0055] Alternatively, a dip coating method can be employed, instead of the spin coating, such that the hexane solution is coated on both sides of the substrate 21 in one operation. Fig. 4 shows an outline configuration of a dip coater 40. With reference to Fig. 4, the substrate 21 is dipped into a tub 41 that is filled with the hexane solution adjusted to a predetermined density for a predetermined period, and then the substrate 21 is pulled up at a fixed speed in the direction of an arrow marked Z. The number of layers of the nanoparticles is controlled by adjusting the speed, and the density of the hexane solution.

[0056] The substrate 21 to which the hexane solution is applied is referred to as a substrate 22. The substrate 22 is dried for about 5 minutes. The self-organization of the nanoparticles of FePt occurs, and the nanoparticles take a multilayer terrace-like super-lattice structure. In this manner, the recording layer 14 having the nanoparticles duly oriented is formed on the non-magnetic middle layer 13. Here, at this stage, since the nanoparticles do not have ferromagnetism at room temperature, the recording layer 14 does not have ferromagnetism.

## (Heat treatment in the magnetic field (Step 107))

[0057] Next, the heat treatment in the magnetic field is performed, using heat-treatment equipment 50. First, the substrate 22, having the recording layer 14 formed, is set in a chamber of the heat treatment equipment,

which is described in detail later. Air in the chamber is exhausted until the atmosphere pressure becomes about  $10^{-5}$  Pa. Then, a predetermined gas is filled to reach a predetermined pressure. Then, the temperature is raised to a predetermined heat-treatment temperature, applying a magnetic field, for a predetermined period. Then, the temperature is lowered.

[0058] Fig. 5 shows an example of the heat treatment equipment 50 for the heat treatment in the magnetic field. Fig. 5 is a sectional view showing a configuration of the heat treatment equipment 50 that employs magnets in the normal condition (i.e., not a superconductivity magnet).

[0059] With reference to Fig. 5, the heat treatment equipment 50 includes two magnets 52 in the normal condition, each of which has a magnetic pole different from each other and counters, two heaters 51 that counter inside the two magnets 52, and a jig (not shown) inside the two heaters, which fixes the substrate 22 on which the recording layer 14 has been formed, and a chamber 53 surrounding the substrate 22. As for the heater 51, a ceramic heater (PBN heater (heat decomposition boron nitride heater)) or a lamp heater is used. Further, the magnets 52 in the normal condition are for uniformly applying a direct-current magnetic field all over the substrate 22.

[0060] The substrate 22 is fixed to the jig, and the direct-current magnetic field is applied to the substrate 22 in the perpendicular direction, e.g., as shown by an arrow marked H in Fig. 5, by the magnets 52 in the normal condition, while the heaters 51 heat the substrate 22.

[0061] Further, the heat treatment equipment may employ a superconductivity magnet instead of the magnet 52 in the normal condition. Fig. 6 is a sectional view showing a configuration of heat treatment equipment 60 that employs the superconductivity magnet.

[0062] With reference to Fig. 6, the heat treatment equipment 60 includes a cylinder-like superconductivity magnet 63, a heater 62 arranged at a central opening of the superconductivity magnet 63, a single disk processing jig (not shown) for arranging the substrate 22 inside the heater 62, and a chamber 61 surrounding the substrate 22. The heater 62 is the same as that of the heater 51 used by the heat treatment equipment 50. The substrate 22 is arranged to the single disk processing jig, and the substrate 22 is heated by the heater 62, while a direct-current magnetic field in the perpendicular direction, e.g., in the direction of arrows marked H shown in Fig. 6, is applied to the substrate 22 by the superconductivity magnet 63.

[0063] Whether the magnetic field is generated by the magnets 52 in the normal condition or by the superconductivity magnet 63, strength of the magnetic field is set between 790 kA/m (10 kOe) and 7900 kA/m (100 kOe). If the magnetic field strength is under 790 kA/m (10 kOe), the hard magnetic nanoparticles 17 are not perpendicularly oriented to a satisfactory degree. If, otherwise, the magnetic field strength is higher than 7900 kA/m,

the superconductivity magnet 63 and the like become large, making the heat treatment equipment impractical.

[0064] The temperature of the heat treatment is set between 200 and 600 degrees C. If the temperature exceeds 600 degrees C, although high coercivity is obtained, substrates, such as a crystallized glass substrate, will soften and the flatness will be deteriorated. Otherwise, if the temperature is lower than 200 degrees C, sufficient coercivity of the hard magnetic nanoparticles 17 cannot be obtained. The temperature of the heat treatment is preferably set at a range between 300 and 500 degrees C. In this temperature range, a tempered glass can be used as the substrate material and degradation of the magnetic characteristic of the soft magnetic lining layer can be prevented.

[0065] For the heat treatment, at least a gas is selected as the atmosphere of the heat treatment from a group of  $N_2$ , He, Ne, Ar, Kr, Xe, and  $H_2$ . With the gas that has inactive or reduction nature, oxidization of the hard magnetic nanoparticles 17 and the magnetic lining layer 12 can be prevented. The gas as the atmosphere for the heat treatment desirably is  $N_2$ .  $N_2$  is considered to form an invaded type alloy with the alloy under process, such as FePt, that constitutes the hard magnetic nanoparticles 17, providing higher perpendicular coercivity than Ar and the like, which allows the heat treatment temperature to be lower.

[0066] Further, the pressure of the gas atmosphere of the heat treatment is preferably set at a range between 1 and  $10^{-6}$  Pa. At a given heat treatment temperature, the higher the pressure is, the greater coercivity of the recording layer 14 is obtained. If the pressure is lower than 1 Pa, the coercivity will not increase. More preferably, the pressure is set at a range between  $10^{-3}$  Pa to  $10^{-6}$  Pa.

[0067] Time of the heat treatment, which is the time during which the temperature is maintained at the predetermined temperature and the magnetic field is applied at the predetermined strength, is set at a range between 10 to 120 minutes. Although the coercivity increases, as the heat treatment time is set longer, the time is preferred to be about 30 minutes from a viewpoint of production efficiency.

45 (Film formation of the overcoat layer 15 (Step 108))

[0068] Next, the overcoat layer 15 is formed on the recording layer 14. For the overcoat layer 15, carbon, carbon hydride, carbon nitride, and the like are used. For example, the overcoat layer 15 of carbon hydride is formed by sputtering the carbon in a mixed atmosphere of Ar gas and  $H_2$  gas, where partial pressure is adjusted by the  $H_2$  gas.

55 (Formation of the lubricous layer 16 (Step 109))

[0069] Next, a lubricant is applied to the overcoat layer 15 so that the lubricous layer 16 is formed. For this

purpose, a lubricant containing perfluoro polyether as the main chain, for example, is used. For example, the lubricous layer is formed by dipping Fomblin AM3001 solution made by Ausimont.

[0070] The perpendicular magnetic memory medium 10 shown in Fig. 1 is formed in the manner mentioned above.

[0071] In the following, embodiments 1 through 7 of the present invention are described, contrasting with comparative examples that are not according to the present invention.

(Embodiment 1)

[0072] The perpendicular magnetic memory medium of the embodiment 1 is structured as shown in Fig. 1, and includes a substrate 11 on the surface of which  $\text{SiO}_2$  is formed by heat oxidizing the surface of Si wafer, a soft magnetic lining layer 12 that consists of 200 nm thick fine crystals of  $\text{FeAlSi}$ , a non-magnetic middle layer 13 that consists of 10 nm thick  $\text{Al}_2\text{O}_3$ , and a recording layer 14 formed by hard magnetic nanoparticles of  $\text{Fe}_{50}\text{Pt}_{50}$ , an overcoat layer 16 that consists of 4 nm thick carbon hydride, and a 1.0 nm thick lubricous layer that consists of Fomblin AM3001.

[0073] The following was performed:

[0074] A heat treatment in a magnetic field after formation of the recording layer 14 was performed in a decompressed  $\text{N}_2$  atmosphere at  $1.5 \times 10^4$  Pa, with a magnetic field of 3950 kA/m (50kOe) applied, for 30 minutes. The heat treatment was performed under three temperature conditions, namely, 460 degrees C, 480 degrees C, and 530 degrees C.

[0075] The average diameter of the hard magnetic nanoparticles 17 of  $\text{Fe}_{50}\text{Pt}_{50}$ , which constitute the recording layer 14, was 6.0nm, the standard deviation of the diameter of the nanoparticles was 8% of the average diameter of the nanoparticles, and the average interval between nanoparticles was 4.0 nm. Here, measurements were performed by photographing an image of the recording layer 14 using HRTEM (high resolution transmission electron microscope). Using the photograph that shows the image expanded by 2 million times, areas of 100 hard magnetic nanoparticles 17 that were photographed were measured. Assuming that the image of each nanoparticle was a circle, diameters of the 100 nanoparticles were obtained, and then, the average diameter of the nanoparticles and the standard deviation of the diameter of the nanoparticles were obtained. The average interval of the hard magnetic nanoparticles 17 was obtained by measuring intervals between the 100 hard magnetic nanoparticles 17.

(Embodiment 2)

[0076] The perpendicular magnetic memory medium of embodiment 2 is constituted like embodiment 1.

[0077] The heat treatment in the magnetic field after

formation of the recording layer 14 was performed in a decompressed Ar atmosphere at  $1.5 \times 10^4$  Pa, with the magnetic field of 3950 kA/m (50kOe) being applied, for 30 minutes. The heat treatment was performed under four temperature conditions, namely, 460 degrees C, 480 degrees C, 530 degrees C, and 560 degrees C.

(Embodiment 3)

[0078] The perpendicular magnetic memory medium of embodiment 3 is constituted like embodiment 1.

[0079] The heat treatment in the magnetic field after formation of the recording layer 14 was performed in a pressurized  $\text{N}_2$  atmosphere at  $2.5 \times 10^5$  Pa, with the magnetic field of 3950 kA/m (50kOe) being applied, for 30 minutes. The heat treatment was performed under two temperature conditions, namely, 360 degrees C and 400 degrees C.

(Embodiment 4)

[0080] The perpendicular magnetic memory medium of embodiment 4 is constituted like embodiment 1.

[0081] The heat treatment in the magnetic field after the formation of the recording layer 14 was performed in a pressurized Ar atmosphere at  $2.5 \times 10^5$  Pa, with the magnetic field of 3950 kA/m (50kOe) being applied, for 30 minutes. The heat treatment was performed under three temperature conditions, namely, 360 degrees C, 400 degrees C, and 430 degrees C.

(Comparative Example 1)

[0082] A perpendicular magnetic memory medium of comparative example 1, which does not belong to the present invention, was constituted like embodiment 1.

[0083] The heat treatment in the magnetic field after formation of the recording layer was performed in vacuum at  $2 \times 10^4$  Pa, with the magnetic field of 3950 kA/m (50kOe) being applied for 30 minutes. The heat treatment was performed under two temperature conditions, namely, 530 degrees C and 580 degrees C.

[0084] Fig. 7 shows relations between the perpendicular coercivity and the heat treatment temperatures. Fig. 7 clearly evidences that the perpendicular coercivity  $H_{c1}$  of the perpendicular magnetic memory medium of the embodiments 1-4 increases as the temperature of the heat treatment gets higher. For example, when the heat treatment temperature of the embodiment 3 was 400 degrees C, the perpendicular coercivity  $H_{c1}$  was 514 kA/m. Under these conditions, in-plane coercivity  $H_{c2}$  in the horizontal direction was measured as 130 kA/m. The ratio of the in-plane (horizontal) coercivity to the perpendicular coercivity  $H_{c2}/H_{c1}$  was, therefore, 25%, indicating that the magnetic easy axis was perpendicular to the substrate.

[0085] In contrast, Fig. 7 shows that the perpendicular coercivity did not increase in the case of the perpendic-

ular magnetic memory medium of the comparative example 1 at the higher heat treatment temperature of 580 degrees C.

[0086] By comparing the embodiment 1 with the embodiment 3, and comparing the embodiment 2 with the embodiment 4, Fig. 7 further evidences that the same perpendicular coercivity is obtained at a lower heat treatment temperature when the pressure of the gas atmosphere is higher for the same gas.

[0087] Further, if embodiment 1 is compared with embodiment 2, or embodiment 3 is compared with embodiment 4, it is evidenced that the N<sub>2</sub> gas atmosphere requires lower heat treatment temperature than the Ar gas atmosphere for the same atmosphere pressure in order to obtain the same perpendicular coercivity.

[0088] Fig. 8 shows relations between lattice constants in the c axis of FePt that constitutes the hard magnetic nanoparticles and heat treatment temperatures. With reference to Fig. 8, the higher the heat treatment temperature was, the smaller the lattice constant of c axis was. Generally, the smaller the lattice constant of c axis of the FePt nanoparticles is, the more the nanoparticles are regularized. Therefore, Fig. 8 indicates that the higher the heat treatment temperature was, the higher the degree of the regularization was. If embodiment 1 is compared with embodiment 3, or embodiment 2 is compared with embodiment 4, it is learned that the lattice constant of c axis was made smaller (that is, the higher regularization was obtained) by the heat treatment in the N<sub>2</sub> gas atmosphere than the Ar gas atmosphere for the same gas pressure. Here, the lattice constants were measured by an X-ray diffraction meter method.

#### (Embodiment 5)

[0089] The perpendicular magnetic memory medium of embodiment 5 is constituted like embodiment 1.

[0090] The heat treatment in the magnetic field after the formation of the recording layer 14 was performed in an N<sub>2</sub> atmosphere, with the magnetic field of 3950 kA/m (50kOe) being applied, for 30 minutes at 530 degrees C. The heat treatment was performed under three gas pressure conditions, namely, 5 Pa, 1.5x10<sup>2</sup> Pa, and 1.5x10<sup>4</sup> Pa.

#### (Comparative example 2)

[0091] A perpendicular magnetic memory medium of comparative example 2, which does not belong to the present invention, was constituted like embodiment 1.

[0092] The N<sub>2</sub> gas pressure was set at 2x10<sup>-4</sup> Pa for the heat treatment in the magnetic field after the formation of the recording layer 14, all other factors remaining the same as those of embodiment 5.

[0093] Fig. 9 shows relations between the perpendicular coercivity of the perpendicular magnetic memory medium of embodiment 5 and comparative example 2,

and the N<sub>2</sub> atmosphere gas pressure. As evident from Fig. 9, comparative example 2 does not provide high perpendicular coercivity, while embodiment 5 provides higher perpendicular coercivity as the N<sub>2</sub> atmosphere gas pressure is made high. It is shown that the perpendicular coercivity increased especially beyond about 1 Pa.

#### (Embodiment 6)

[0094] The perpendicular magnetic memory medium of embodiment 6 was constituted like embodiment 1.

[0095] The heat treatment in the magnetic field after the formation of the recording layer 14 was performed in a decompressed N<sub>2</sub> atmosphere at 1.5x10<sup>4</sup> Pa, with the magnetic field of 3950 kA/m (50kOe) being applied, at 460 degrees C for 30 minutes.

#### (Embodiment 7)

[0096] The perpendicular magnetic memory medium of embodiment 7 was constituted like embodiment 1.

[0097] The heat treatment in the magnetic field after the formation of the recording layer 14 was performed in a pressurized N<sub>2</sub> atmosphere at 2.5x10<sup>5</sup> Pa, with the magnetic field of 3950 kA/m (50kOe) being applied, at 460 degrees C for 30 minutes.

[0098] Fig. 10 shows an X-ray diffraction pattern of the perpendicular magnetic memory medium of embodiments 6 and 7. With reference to Fig. 10, peaks of the face-centered tetragonal (fct) lattices of an FePt ordered alloy are shown, which indicate that desired regularization of the FePt ordered alloy was obtained by the embodiments 6 and 7. Especially, embodiment 7, which is expressed by the upper plot in Fig. 10, using the higher gas pressure in the heat treatment, obtained sharper peaks, i.e., higher regularization degree, than embodiment 6, using the lower gas pressure, which is expressed by the lower plot.

[0099] Next, an embodiment of a magnetic memory storage of the present invention is explained with reference to Fig. 11 and Fig. 12. Fig. 11 is a sectional view showing the principal part of the magnetic memory storage of the embodiment. Fig. 12 is a plane view showing the principal part of the magnetic memory storage of the embodiment.

[0100] As shown in Fig. 11 and Fig. 12, the magnetic memory storage 120 includes a motor 124, a hub 125, two or more perpendicular magnetic memory media 126, two or more recording and reproducing heads 127, two or more suspensions 128, two or more arms 129, and an actuator unit 121, all of which are housed in a housing 123. The perpendicular magnetic memory media 126 are attached to the hub 125 that is rotated by the motor 124. The recording and reproducing heads 127 are compounded type heads where the recording heads employ a thin film head, and the reproducing heads employ an MR element (magnetic resistance ef-

fect type element), a GMR element (great magnetic resistance effect type element), or a TMR element (tunnel magnetism effect type element). The recording heads may use a monopole magnetic head, or a ring type head. Each of the recording and reproducing heads 127 is attached at the tip of the corresponding arm 129 through the suspension 128. The arm 129 is driven by the actuator unit 121. The basic composition of this magnetic memory storage itself is common knowledge, and the detailed explanation thereof is omitted.

[0101] The magnetic memory storage 120 of the present embodiment is characterized by installing the perpendicular magnetic memory media 126 of the embodiments 1-7 of the present invention, having a layered structure as shown in Fig. 1. The number of the perpendicular magnetic memory media 126 is not limited to three, but any number of perpendicular magnetic memory media may be used.

[0102] The basic composition of the magnetic memory storage 120 is not limited to what is shown in Fig. 11 and Fig. 12. The perpendicular magnetic memory media 126 used by the present invention are not limited to magnetic disks.

[0103] Although preferred embodiments of the present invention are explained in full detail in the above, various variations and modifications may be made without departing from the scope of the present invention.

[0104] In addition, although the embodiments of the present invention are explained, where the perpendicular magnetic memory medium has a soft magnetic lining layer 12 and a non-magnetic middle layer 13, these items are not indispensable. For example, the soft magnetic lining layer 12 is formed according to the method of a recording head, for example, a single magnetic pole head method. Further, a configuration that does not include the soft magnetic lining layer 12 and the non-magnetic middle layer 13 has proven that its characteristics are similar to the characteristics shown in Fig. 8 through Fig. 11 about embodiments 1-7.

[0105] As described in detail in the above, the present invention provides a perpendicular magnetic memory medium capable of high-density recording and reproducing and a manufacturing method thereof that gives perpendicular magnetic orientation to hard magnetic nanoparticles without deteriorating the flatness of the substrate and the soft magnet characteristics of the soft magnetic lining layer.

[0106] Further, the present invention is not limited to these embodiments, but various variations and modifications may be made without departing from the scope of the present invention.

[0107] The present application is based on Japanese priority application No.2002-168411 filed on June 10, 2002 with the Japanese Patent Office, the entire contents of that are hereby incorporated by reference.

## Claims

1. A perpendicular magnetic memory medium comprising a recording layer that is formed by arranging hard magnetic nanoparticles on a substrate, wherein an average diameter of the hard magnetic nanoparticles is between 2nm and 10nm, a standard deviation of diameters of the hard magnetic nanoparticles is 10% or less of the average diameter of the hard magnetic nanoparticles, an average interval between the hard magnetic nanoparticles is between 0.2nm and 5nm, and an magnetic easy axis of the recording layer is perpendicular to a surface of the substrate.
2. The perpendicular magnetic memory medium as claimed in claim 1, wherein the hard magnetic nanoparticles contain at least two or more elements selected from the group consisting of Fe, Co, Ni, Pt, and Pd.
3. The perpendicular magnetic memory medium as claimed in claim 1 or 2, wherein a soft magnetic lining layer is provided between the substrate and the recording layer, the soft magnetic lining layer containing at least one element selected from the group consisting of Fe, Co, Ni, Al, Si, Ta, Ti, Zr, Hf, V, Nb, C, and B.
4. A manufacturing method of a perpendicular magnetic memory medium that has a recording layer formed by arranging hard magnetic nanoparticles on a substrate, comprising a process of heat treatment in a magnetic field, wherein the recording layer is heated in a gas atmosphere, while a magnetic field is applied perpendicularly to the recording layer, the process of heat treatment in the magnetic field making a magnetic easy axis of the recording layer perpendicular to a surface of the substrate.
5. The manufacturing method of the perpendicular magnetic memory medium as claimed in claim 4, wherein temperature used in the process of heat treatment in the magnetic field is decreased as the pressure of the gas atmosphere is increased.
6. The manufacturing method of the perpendicular magnetic memory medium as claimed in claim 4 or 5, wherein a magnitude of the magnetic field of the process is set between 790 kA/m and 3950 kA/m, pressure of the gas atmosphere of the process is set between  $10^{+3}$  to  $10^{+6}$  Pa, and temperature of the process is set between 200 degrees C and 600 degrees C.
7. The manufacturing method of the perpendicular magnetic memory medium as claimed in claim 4, 5 or 6, wherein gas of the gas atmosphere used in the

process is at least one selected from the group consisting of N<sub>2</sub>, He, Ne, Ar, Kr, Xe, and H<sub>2</sub>.

8. A magnetic memory storage, comprising the perpendicular magnetic memory medium as claimed in 5  
claim 1, 2 or 3.

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FIG.1

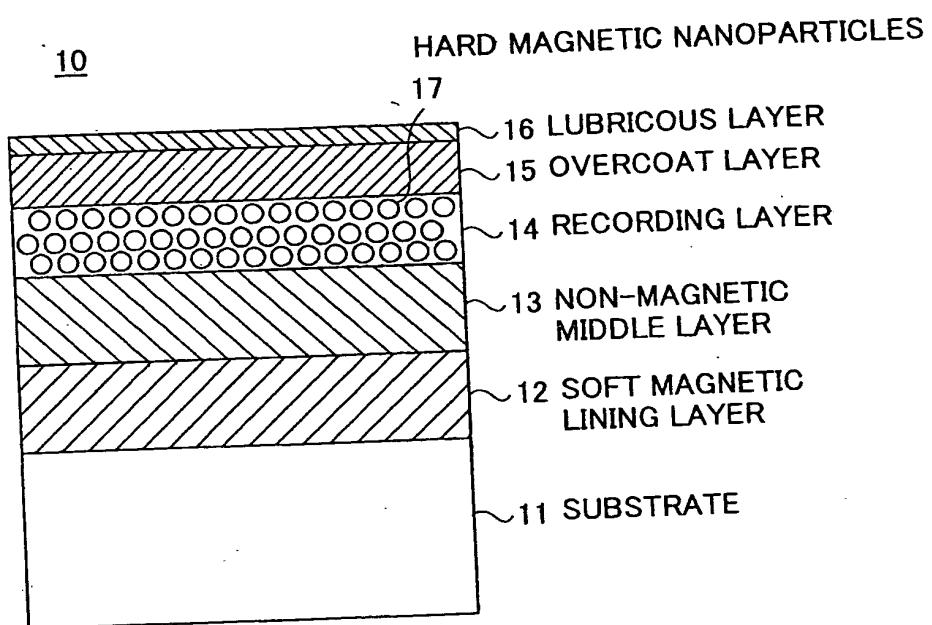


FIG.2

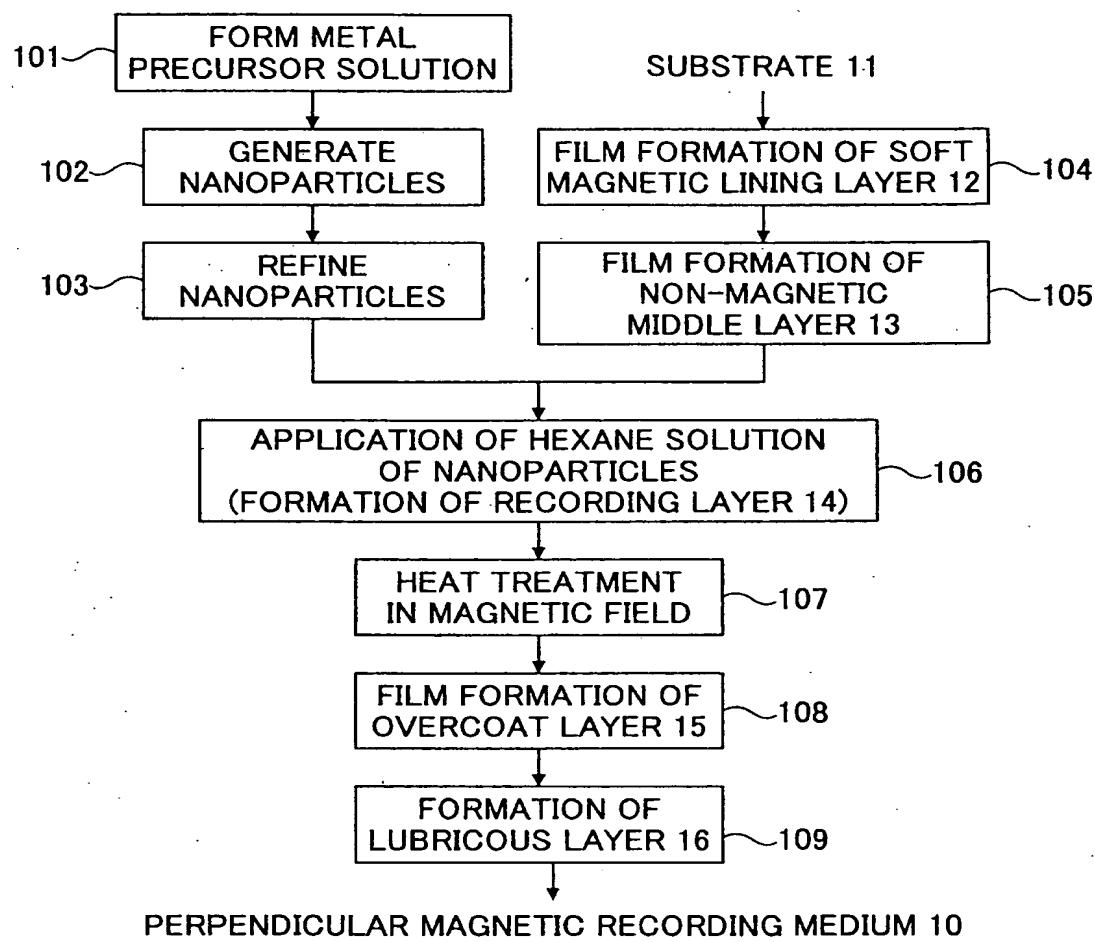


FIG.3

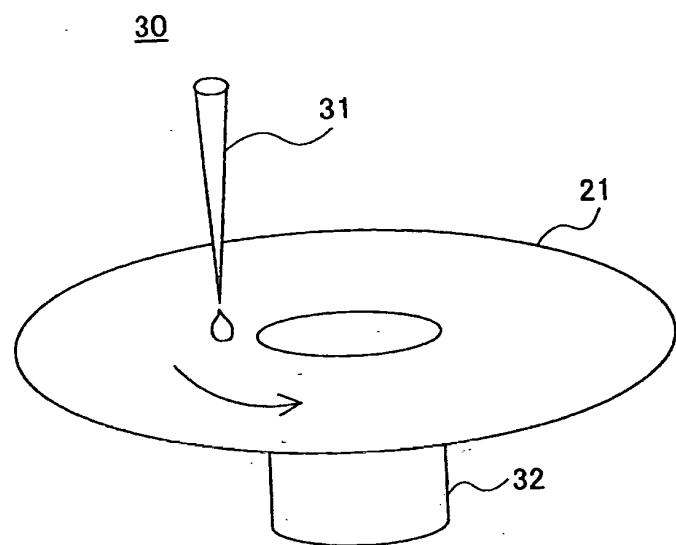


FIG.4

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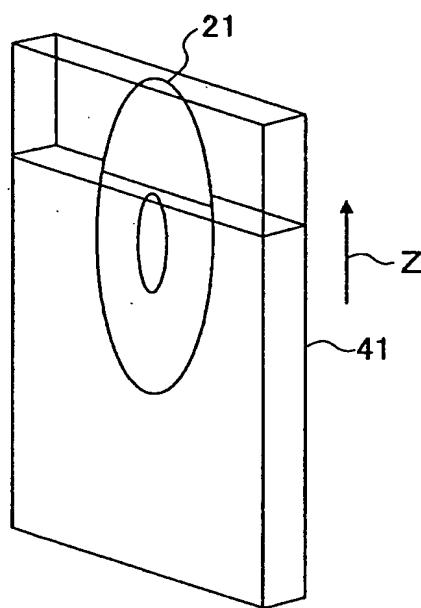


FIG.5

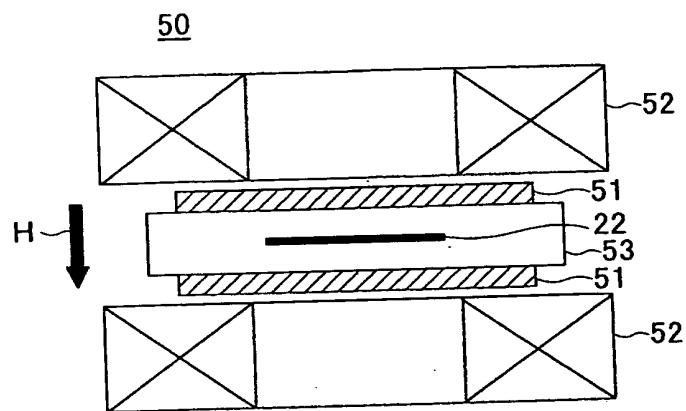


FIG.6

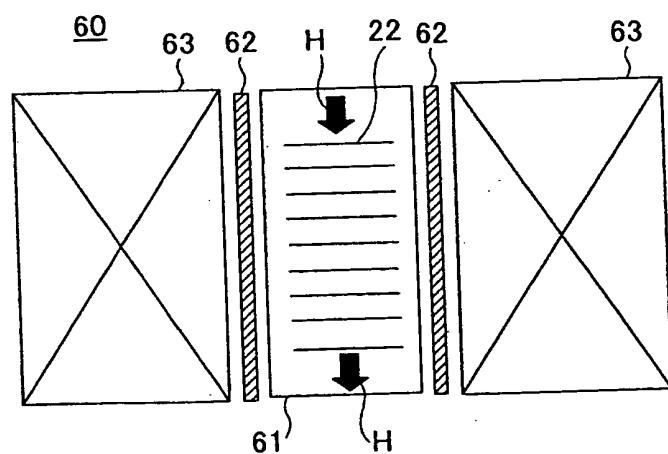


FIG. 7

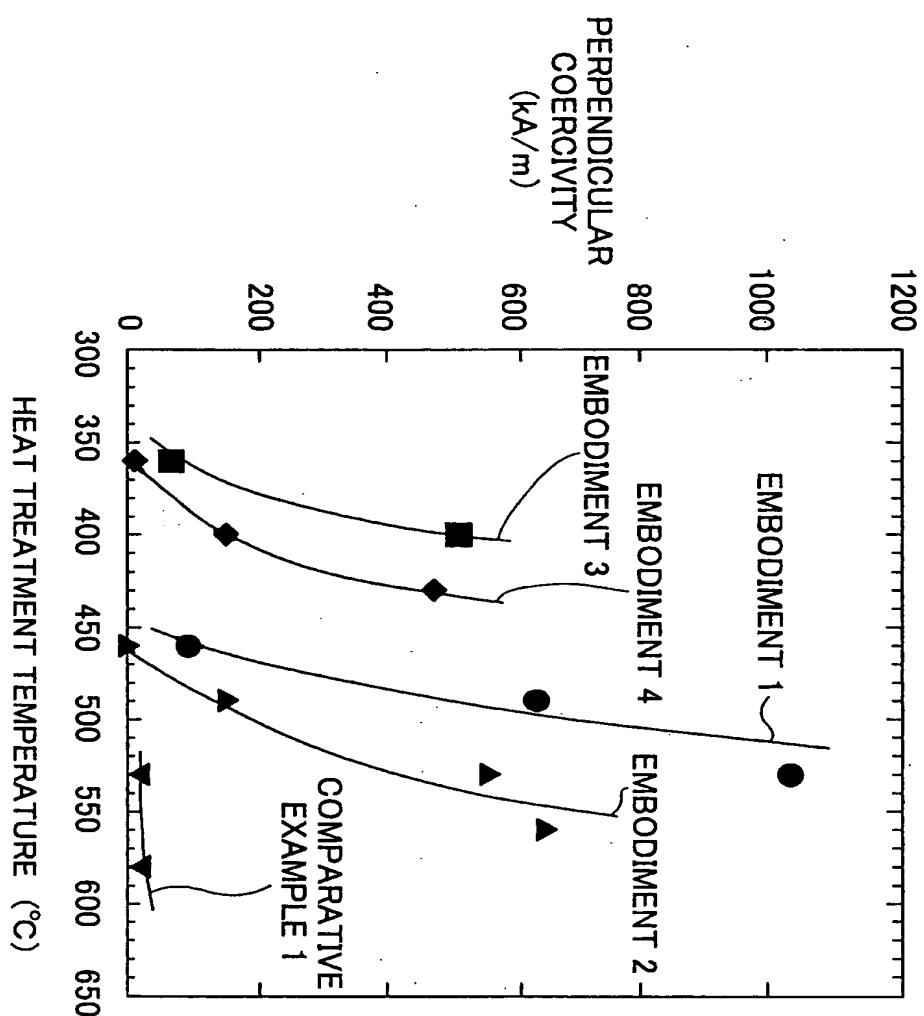
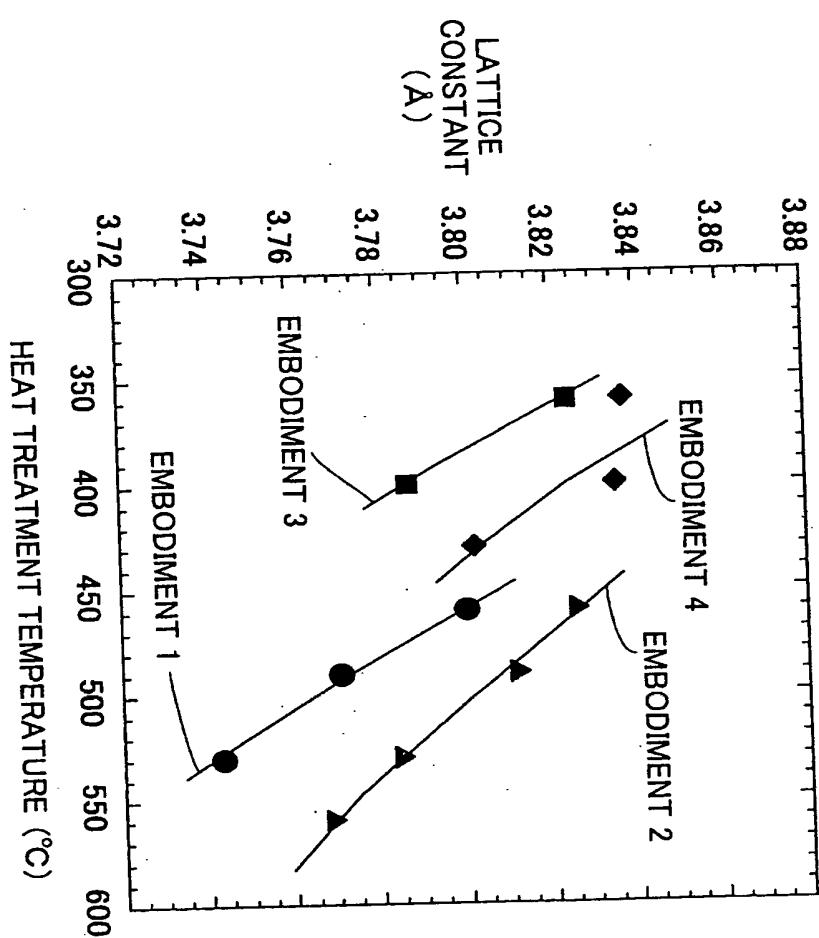
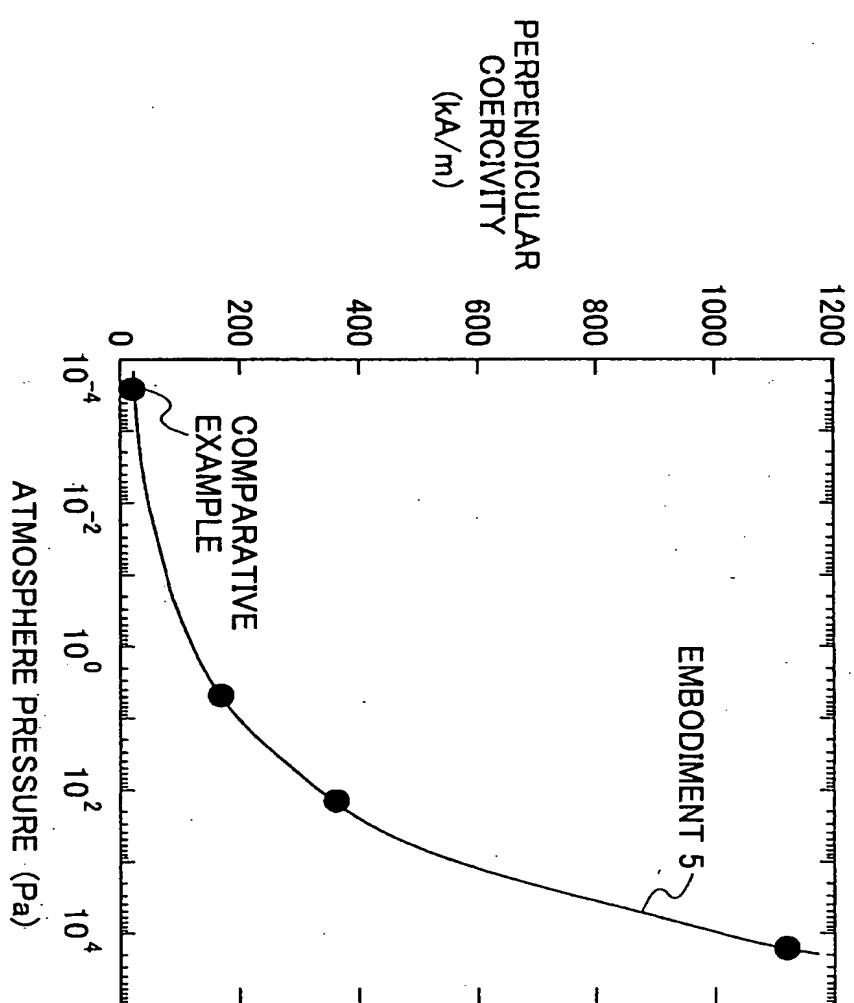


FIG.8





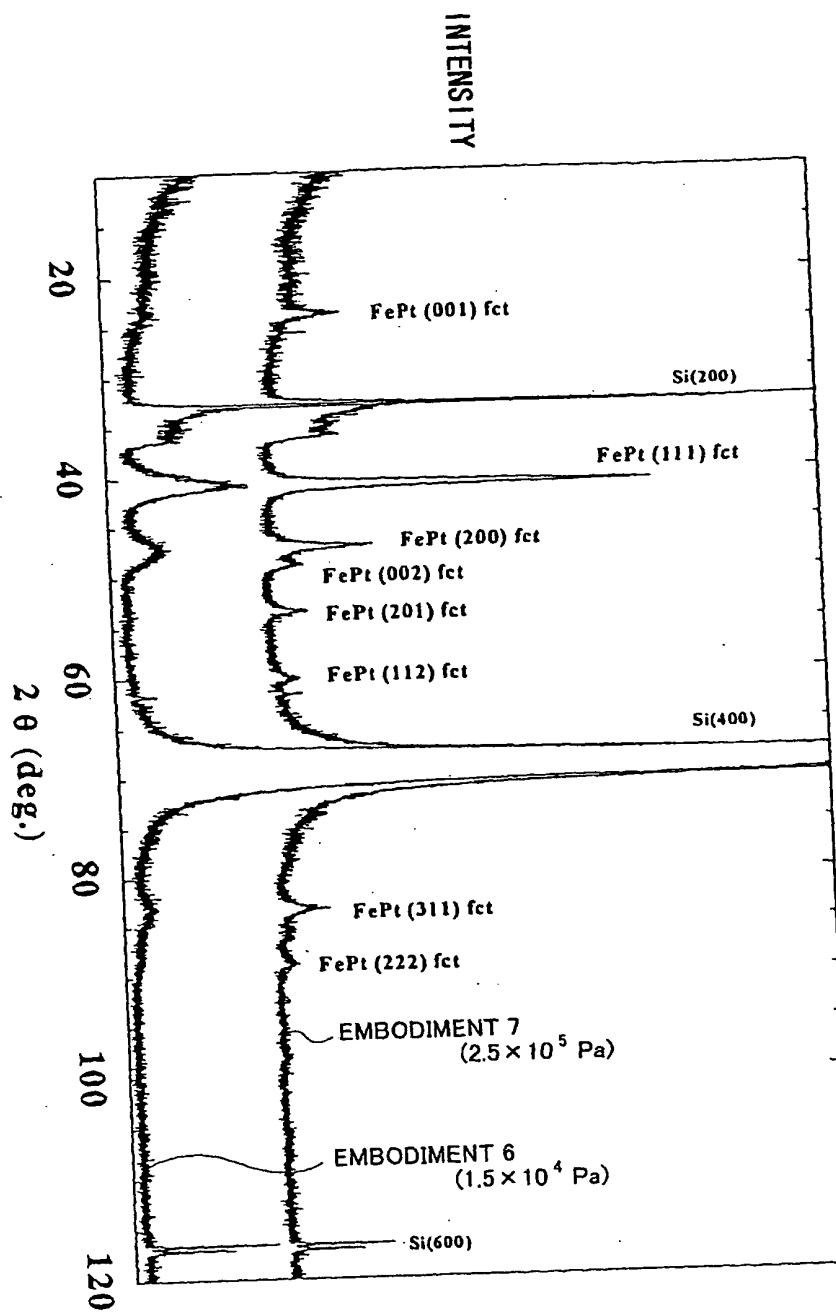


FIG.10

FIG. 11

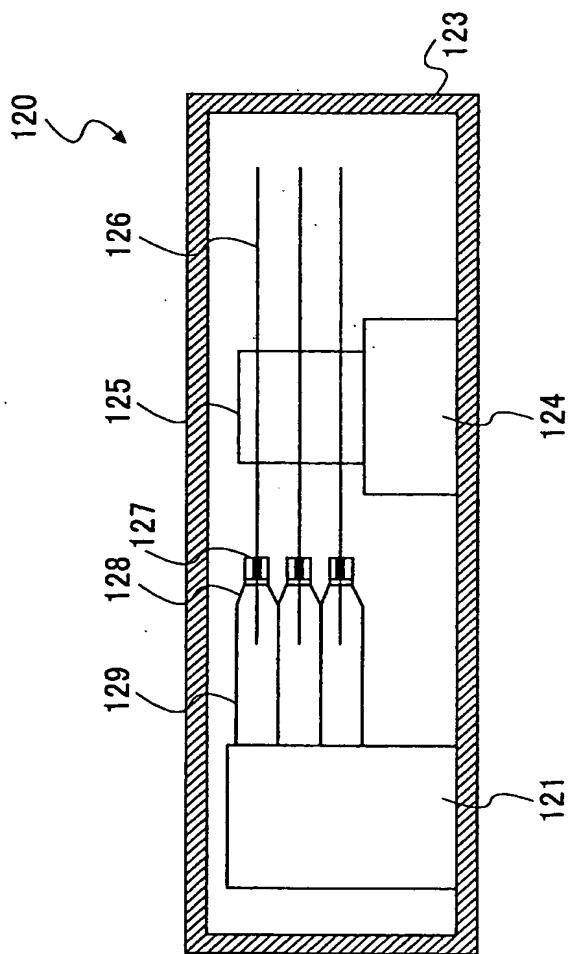
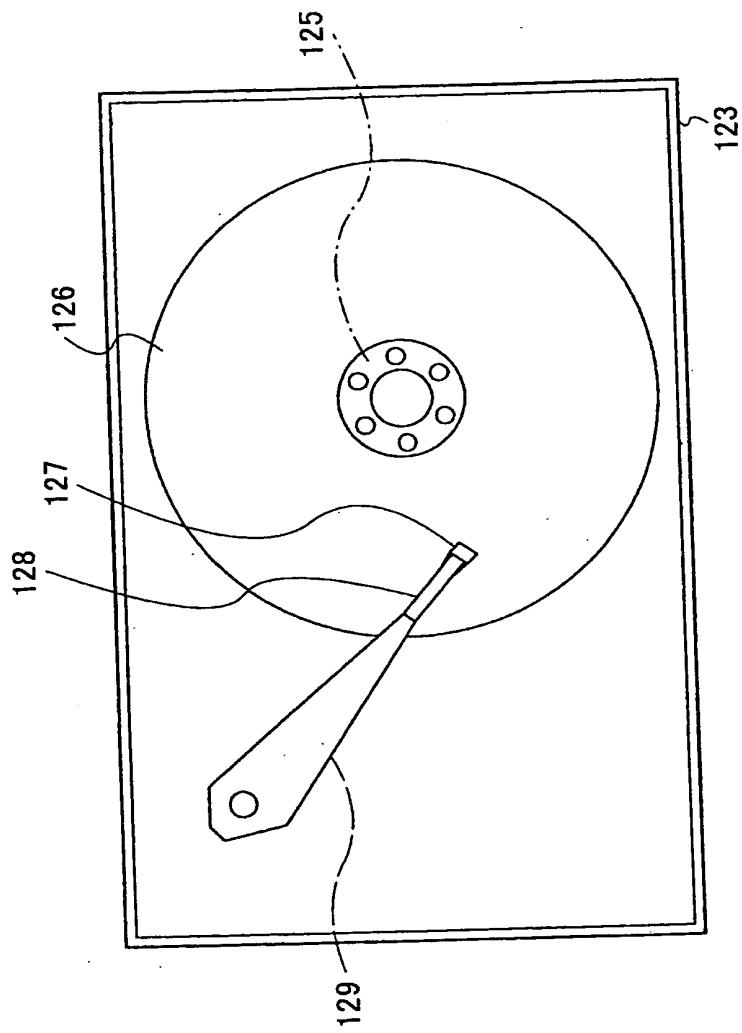


FIG.12





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 03 00 8035

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	19 June 2003	Magrizos, S	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 03 00 8035

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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19-06-2003

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